

PERCHLORATE ON MARS – OVERVIEW AND IMPLICATIONS. P.D. Archer, Jr¹, D.W. Ming², B. Sutter¹, J.V. Hogan³, R.V. Morris², B.C. Clark⁴, P.H. Mahaffy⁵, R. Navarro-González⁶, C.P. McKay⁷, R.V. Gough⁸, and A.G. Fairen⁹, ¹Jacobs, NASA Johnson Space Center, Houston, TX, 77058, doug.archer@nasa.gov, ²NASA Johnson Space Center, Houston, TX, ³Geocontrols Systems – Jacobs JETS Contract, NASA Johnson Space Center, ⁴Space Science Institute, Boulder, CO 80301, ⁵NASA Goddard Space Flight Center, Greenbelt, MD 20771 ⁶Instituto de Ciencias Nucleares, UNAM, Mexico City, Mexico, ⁷NASA Ames Research Center, Moffett Field, CA 94035, ⁸University of Colorado, Boulder, CO 80309, ⁹Centro de Astrobiología (INTA-CSIC), Madrid, Spain.

Introduction: Perchlorate was first detected on Mars by the Wet Chemistry Laboratory (WCL) instrument on the Phoenix lander at a concentration of ~0.5 wt% in northern plains soils [1]. Since that initial detection, perchlorate (and likely chlorate) have been detected on Mars by both surface and orbital instruments [2, 3]. Perchlorate (ClO_4^-) is an oxidized chlorine compound and salts of perchlorate are kinetically stable (though very reactive at high temperature), very soluble, deliquescent, and have low eutectic temperature (which decreases the temperature for stable liquids on Mars). Chlorate (ClO_3^-) salts are similar, though they are less kinetically stable than perchlorates [4, 5]. Because many of the analytical signatures of perchlorate and chlorate are similar to the instruments we have used on Mars, we cannot always determine which species is present, so we will use the more generic term “oxychlorine” when referring to perchlorate and/or chlorate.

Oxychlorines on Mars: In addition to detection in soils at the northern plains of Mars by the Phoenix lander, oxychlorines have been detected at many other locations on the martian surface. First, data from the GCMS and life detection instruments on the Viking landers have been used to infer the presence of perchlorate at both landing sites [6, 7]. Oxychlorines have been detected by the Sample Analysis at Mars (SAM) instrument on the Mars Science Laboratory (MSL) lander in multiple Gale Crater samples, including all Aeolian/soil samples, and in both mudstones and sandstones. Perchlorate has been detected from orbit in multiple locations, including associated with RSLs, though some of these detections have been disputed [3, 8]. Finally, perchlorate has been definitively detected at low levels in at least one martian meteorite [9].

Terrestrial Comparison: Perchlorates have also been detected in multiple locations on Earth, generally in arid environments [e.g., 10, 11]. These perchlorates are produced in the stratosphere, based on their $\Delta^{17}\text{O}$ values, and generally occur at much lower concentrations than on Mars (10s to 100s of ppb on Earth vs. up to ~1 wt% on Mars). Additionally, on earth the chlorate:perchlorate ratio is generally ≥ 1 . On Mars, we know from Phoenix data that the ratio is

< 1. MSL does not have the ability to definitively disentangle perchlorate from chlorate, because the temperature at which the oxychlorine decomposes and releases O_2 (the main difference between perchlorates and chlorates in evolved gas analysis by SAM) can be complicated by the presence of other minerals which can catalyze decomposition [12, 13]. Even accounting for that uncertainty, it is likely that both perchlorate and chlorate have been detected in Gale crater samples.

Terrestrial perchlorate is primarily destroyed through biologically mediated reduction pathways [14], although chlorates could also be reduced by Fe(II) minerals, which is also relevant to Mars.

Formation mechanisms on Mars: As previously stated, terrestrial perchlorate is produced in the stratosphere through reactions of Cl with ozone. This formation mechanism was considered for Mars but was modeled to be orders of magnitude too slow to explain the observed perchlorate abundances [15, 16]. Other formation mechanisms that have been proposed include oxidation at grain surfaces mediated by a mineral catalyst and UV light [17, 18], atmospheric formation with production enhanced by OClO produced by radiolysis of surface materials [19], and through reactions with free radicals produced by electrostatic discharge in a martian dust storm [20, 21]. Research into the various formation mechanisms is ongoing. For all of these models, the source of the Cl is from volcanic exhalations [22] and/or Cl released through the aqueous weathering of basaltic material [23]. The O_2 is atmospheric for the UV-mediated and electrostatic discharge model and comes both the atmosphere and minerals in the radiolysis model.

Implications: The presence and/or varied concentration of oxychlorine compounds on Mars has various implications. First, if perchlorates formed throughout martian history, their relative concentration could be a signature of different environmental conditions or processes such as changes in the martian atmosphere or changes in aqueous activity (i.e. amount of precipitation) [24]. Second, as mentioned previously, perchlorate/chlorate brines have low eutectic temperatures and can be extremely deliquescent, depending on the cation. This increases the probability for liquid water to exist on the martian

surface. These perchlorate-rich brines have been proposed as one of the factors that cause (or allow for) Recurring Slope Lineae (RSL), by allowing liquid water over a wider range of expected martian surface temperatures [25]. However, recent work has indicated that RSL may be caused by a dry granular flow mechanism [26], but volume changes of deliquescing and efflorescing perchlorate salts [27] could be one mechanism of initiating a dry debris flow.

The possibility for perchlorate-rich liquid brines has been cited by many studies as being important to life on Mars since liquid water is a prerequisite for life as we know it. However, it is not clear how relevant this is to potential life because the water activity (a_w) of such a concentrated brine is well below the a_w necessary for life as we know it [28]. Additionally, since biologically induced reduction is a primary pathway for perchlorate removal on the earth, the accumulation of perchlorates on Mars to levels orders of magnitude higher than terrestrial values could be a sort of reverse biosignature, indicating that perchlorate-reducing life never existed on Mars, at least not in the near surface environment.

Oxychlorine species are also relevant to the detection of organic molecules on Mars. If an organic detection instrument uses pyrolysis to liberate native organic compounds, these products can react with the decomposition products of oxychlorines—O₂ (combustion) and Cl (chlorination)—which either destroy the organic completely, or alter its chemical composition. This likely occurred in the Viking GCMS instruments [6] and has definitely occurred in the SAM instrument on MSL [29].

Finally, oxychlorine species are relevant to the human exploration of Mars for two primary reasons: human health considerations and *in situ* resource utilization (ISRU) [30]. Perchlorate is relevant to human health because it is toxic in large doses or through prolonged exposure because it competes with iodide uptake in the thyroid, decreasing thyroid function [31]. However, the levels of perchlorate in the martian dust are low enough that filtration is sufficient to mitigate this risk. Perchlorates are a potential resource for ISRU from the standpoint of both water and oxygen; water because perchlorate is so deliquescent it can suck water out of the martian atmosphere that is released when the perchlorate is heated to ~200 °C, and oxygen, because perchlorates decompose and release a significant amount of oxygen when heated to 200-500 °C (the exact temperature depends on the cation, chlorate vs. perchlorate, and the presence of other catalytic minerals). Thus, perchlorates can be a potential resource for future Mars exploration.

Conclusions: Perchlorates have been detected both from orbit and on the surface at many different locations on Mars at concentrations orders of magnitude higher than is seen for naturally occurring perchlorate on the earth. The formation mechanism for these oxychlorine species remains an active area of research, as does explaining the variability of oxychlorine species on Mars.

References: [1] Hecht M. H. et al. (2009) *Science*, 325, 64-67. [2] Glavin D. P. et al. (2013) *JGR: Planets*, 118, 1955-1973. [3] Ojha L. et al. (2015) *Nature Geoscience*, 8, 829-832. [4] Mitra K. et al. (2019) LPS L, Abstract #1296. [5] Brundrett M. et al. (2019) *ACS Earth and Space Chemistry*. [6] Navarro-González R. et al. (2010), *JGR*, 115, E12010. [7] Quinn R. C. et al. (2013) *Astrobiology*, 13, 515-520. [8] Leask E. K. et al. (2018) *GRL*, 45, 12,180-112,189. [9] Jaramillo E. A. et al. (2019) *GRL*, 46, 3090-3098. [10] Jackson W. A. et al. (2016) *GCA*, 182, 197-215. [11] Jackson W. A. et al. (2015) *GCA*, 164, 502-522. [12] Hogancamp J. V. et al. (2018) *JGR: Planets*, 123, 2920-2938. [13] Sutter B. et al. (2015) LPS XLVI, Abstract #2137. [14] Lynch K. L. et al. (2019) *Astrobiology*, 19, 629-641. [15] Dasgupta P. K. et al. (2005) *Environ Sci Technol*, 39, 1569-1575. [16] Smith M. L. et al. (2014) *Icarus*, 231, 51-64. [17] Carrier B. L. et al. (2015) *GRL*, 42, 3739-3745. [18] Schuttlefield J. D. et al. (2011) *J of the Amer. Chem. Society*, 133, 17521-17523. [19] Wilson E. H. et al. (2016), *JGR: Planets*, 121, 1472-1487. [20] Wu Z. et al. (2018) *EPSL*, 504, 94-105. [21] Martínez-Pabello P. U. et al. (2019) *Life Sciences in Space Research*. [22] Keller J. M. et al. (2006) *JGR*, 111, E03S08. [23] Filiberto J. et al. (2009) *Geology*, 37, 1087-1090. [24] Archer P. D. Jr. et al. (2019) LPS L, Abstract #3041. [25] Heinz J. et al. (2016) *GRL*, 43, 4880-4884. [26] Dundas C. M. et al. (2017) *Nature Geoscience*, 10, 903-907. [27] Gough R. V. et al. (2019) *Icarus*, 321, 1-13. [28] Al Soudi A. F. et al. (2017) *Int J Astrobiol* 16, 229-235. [29] Freissinet C. et al. (2015) *JGR: Planets*, 120, 2014JE004737. [30] Davila A. F. et al. (2013) *Int J Astrobiol*, 12, 321-325. [31] Wolff J. (1998) *Pharmacological Reviews*, 50, 89-106.